US009067192B2

(12) **United States Patent**
Yang et al.

(10) **Patent No.: US 9,067,192 B2**
(45) **Date of Patent: *Jun. 30, 2015**

(54) **POLLUTANT EMISSION CONTROL SORBENTS AND METHODS OF MANUFACTURE AND USE**

(71) Applicant: **BASF Corporation**, Florham Park, NJ (US)

(72) Inventors: **Xiaolin David Yang**, Edison, NJ (US); **Pascaline Harrison Tran**, Holmdel, NJ (US); **Lawrence Shore**, Jerusalem (IL)

(73) Assignee: **BASF CORPORATION**, Florham Park, NJ (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **14/175,497**

(22) Filed: **Feb. 7, 2014**

(65) **Prior Publication Data**

US 2014/0151599 A1 Jun. 5, 2014

Related U.S. Application Data

(63) Continuation of application No. 12/707,450, filed on Feb. 17, 2010, now Pat. No. 8,685,351, which is a continuation-in-part of application No. 12/329,246, filed on Dec. 5, 2008, now Pat. No. 8,906,823, which is a continuation-in-part of application No. 11/860,148, filed on Sep. 24, 2007.

(51) **Int. Cl.**

B01D 53/64 (2006.01)
B01J 20/04 (2006.01)

(Continued)

(52) **U.S. Cl.**

CPC ***B01J 20/18*** (2013.01); ***B01D 53/64*** (2013.01); *B01D 2251/304* (2013.01);

(Continued)

(58) **Field of Classification Search**

CPC B01J 2220/42
USPC 502/400, 407, 412, 415, 416, 417
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,663,165 A 5/1972 Haden, Jr. et al.
3,793,185 A 2/1974 Whitehurst et al.

(Continued)

FOREIGN PATENT DOCUMENTS

EP 0043759 A1 1/1982
EP 0145539 6/1985

(Continued)

OTHER PUBLICATIONS

Control of Mercury Emissions From Coal-Fired Electric Utility Boilers, *EPA Report*, EPA-600/R-01-109 Apr. 2002.

(Continued)

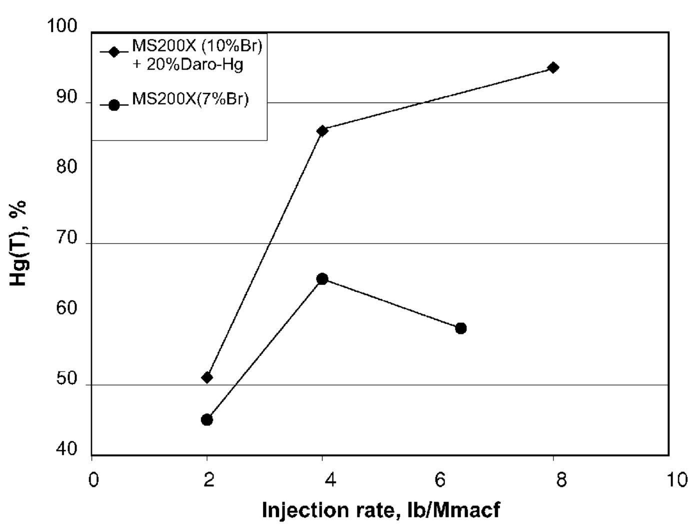
Primary Examiner — Wayne Langel

(74) *Attorney, Agent, or Firm* — Lowenstein Sandler LLP

(57) **ABSTRACT**

Sorbents for removal of mercury and other pollutants from gas streams, such as a flue gas stream from coal-fired utility plants, and methods for their manufacture and use are disclosed. Embodiments include brominated sorbent substrate particles having a carbon content of less than about 10%. Other embodiments include one or more oxidatively active halides of a nonoxidative metal dispersed on sorbent substrate particles mixed with activated carbon in an amount up to 30% by weight. Further embodiments include physical blending of a flow modifier into the sorbent composition.

16 Claims, 4 Drawing Sheets



(51) **Int. Cl.**

B01J 20/18	(2006.01)
B01J 20/02	(2006.01)
B01J 20/28	(2006.01)
B01J 20/30	(2006.01)
B01J 20/32	(2006.01)
B01J 20/12	(2006.01)

(52) **U.S. Cl.**
CPC *B01D 2251/60* (2013.01); *B01D 2257/602* (2013.01); ***B01J 20/0244*** (2013.01); ***B01J 20/0288*** (2013.01); ***B01J 20/046*** (2013.01); ***B01J 20/28057*** (2013.01); ***B01J 20/3085*** (2013.01); ***B01J 20/3204*** (2013.01); ***B01J 20/3236*** (2013.01); *B01J 2220/42* (2013.01); ***B01J 20/027*** (2013.01); ***B01J 20/043*** (2013.01); ***B01J 20/12*** (2013.01)

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,094,777	A	6/1978	Sugier et al.
4,120,782	A	10/1978	Audeh et al.
4,493,902	A	1/1985	Brown et al.
4,699,893	A	10/1987	Andrews et al.
4,708,853	A	11/1987	Matviya et al.
4,895,638	A	1/1990	Aufdembrink et al.
4,902,662	A	2/1990	Toulhoat et al.
5,306,474	A	4/1994	Kida et al.
5,405,593	A	4/1995	Knudson
5,409,522	A	4/1995	Durham et al.
5,472,594	A	12/1995	Tsang et al.
5,505,766	A	4/1996	Chang
5,569,436	A	10/1996	Lerner
5,607,496	A	3/1997	Brooks
5,618,508	A	4/1997	Suchenwirth et al.
5,695,726	A	12/1997	Lerner
5,702,589	A	12/1997	Tsang et al.
5,827,352	A	10/1998	Altman et al.
5,854,173	A	12/1998	Chang et al.
5,868,829	A	2/1999	Biermann et al.
5,897,688	A	4/1999	Voogt et al.
5,948,143	A	9/1999	Sjostrom et al.
6,027,551	A	2/2000	Hwang et al.
6,136,072	A	10/2000	Sjostrom et al.
6,375,909	B1	4/2002	Dangtran et al.
6,521,021	B1	2/2003	Pennline et al.
6,558,454	B1	5/2003	Chang et al.
6,638,485	B1	10/2003	Iida et al.
6,656,347	B2	12/2003	Stockwell et al.
6,673,235	B2	1/2004	Harris et al.
6,695,894	B2	2/2004	Chang et al.
6,712,878	B2	3/2004	Chang et al.
6,719,828	B1	4/2004	Lovell et al.
6,770,250	B2	8/2004	Cooper et al.
6,808,692	B2	10/2004	Oehr
6,818,043	B1	11/2004	Chang et al.
6,953,494	B2	10/2005	Nelson, Jr.
7,048,781	B1	5/2006	Lovell
7,276,152	B2	10/2007	Lin et al.
8,226,913	B2	7/2012	Comrie
8,313,323	B2	11/2012	Comrie
8,313,543	B2	11/2012	Nalepa
8,685,351	B2 *	4/2014	Yang et al. 423/210
2003/0103882	A1	6/2003	Biermann et al.
2003/0104937	A1	6/2003	Sinha
2003/0118493	A1	6/2003	Cooper et al.
2003/0176396	A1	9/2003	Shea et al.
2003/0206843	A1	11/2003	Nelson
2004/0003716	A1	1/2004	Nelson
2004/0081606	A1	4/2004	Cooper et al.
2004/0202596	A1	10/2004	Honjo et al.
2005/0129597	A1	6/2005	Cross et al.
2005/0181931	A1	8/2005	Mouri et al.
2005/0199554	A1	9/2005	Goolsby et al.
2006/0205592	A1	9/2006	Chao et al.
2006/0210463	A1	9/2006	Comrie
2006/0230930	A1	10/2006	Knaebel
2007/0119300	A1	5/2007	Yang et al.
2007/0122327	A1	5/2007	Yang et al.
2007/0122619	A1	5/2007	Yang et al.
2007/0140940	A1	6/2007	Varma et al.
2007/0289447	A1	12/2007	Yang et al.
2007/0292328	A1	12/2007	Yang et al.
2008/0210599	A1	9/2008	O'Connor et al.
2009/0136401	A1	5/2009	Yang et al.

FOREIGN PATENT DOCUMENTS

EP	0271618		6/1988
EP	0480603	A2	4/1992
EP	0484234	A2	5/1992
EP	0930091		7/1999
GB	2124249	A	2/1984
WO	WO-0185307		11/2001
WO	WO-2007/149833		12/2007
WO	WO-2007/149837		12/2007

OTHER PUBLICATIONS

Final Office Action in U.S. Appl. No. 11/860,148, mailed Mar. 16, 2011, 16 pages.

Final Office Action in U.S. Appl. No. 11/860,148, mailed May 9, 2012, 10 pages.

Final Office Action in U.S. Appl. No. 12/329,246, dated Jan. 6, 2012, 14 pages.

Final Office Action in U.S. Appl. No. 12/707,450, dated Aug. 15, 2013, 6 pages.

Final Office Action in U.S. Appl. No. 12/707,450, mailed Dec. 13, 2012, 10 pages.

Final Office Action in U.S. Appl. No. 12/329,246, dated Mar. 5, 2013, 16 pages.

Non-Final Office Action in U.S. Appl. No. 11/860,148, dated Oct. 5, 2010, 12 pages.

Non-Final Office Action in U.S. Appl. No. 11/860,148, mailed Oct. 7, 2011, 11 pages.

Non-Final Office Action in U.S. Appl. No. 12/329,246, dated Feb. 3, 2014, 13 pages.

Non-Final Office Action in U.S. Appl. No. 12/329,246 dated Jun. 28, 2012, 11 pages.

Non-Final Office Action in U.S. Appl. No. 12/329,246, mailed Mar. 24, 2011, 17 pages.

Non-Final Office Action in U.S. Appl. No. 12/707,450, mailed Apr. 25, 2013, 8 pages.

Non-Final Office Action in U.S. Appl. No. 12/707,450, mailed Aug. 24, 2012, 18 pages.

Non-Final Office Action in U.S. Appl. No. 13/566,521 dated Dec. 24, 2012, 13 pages.

Non-Final Office Action in U.S. Appl. No. 13/566,521, mailed Dec. 24, 2012, 13 pages.

PCT/US2006/0044711—PCT International Search Report, 3 pages.

Grantie, Evan J. et al., Novel Sorbents for Mercury Removal from Flue Gas, *Ing. Eng. Chem. Res.*, 39 2000 , 1020-1029.

* cited by examiner

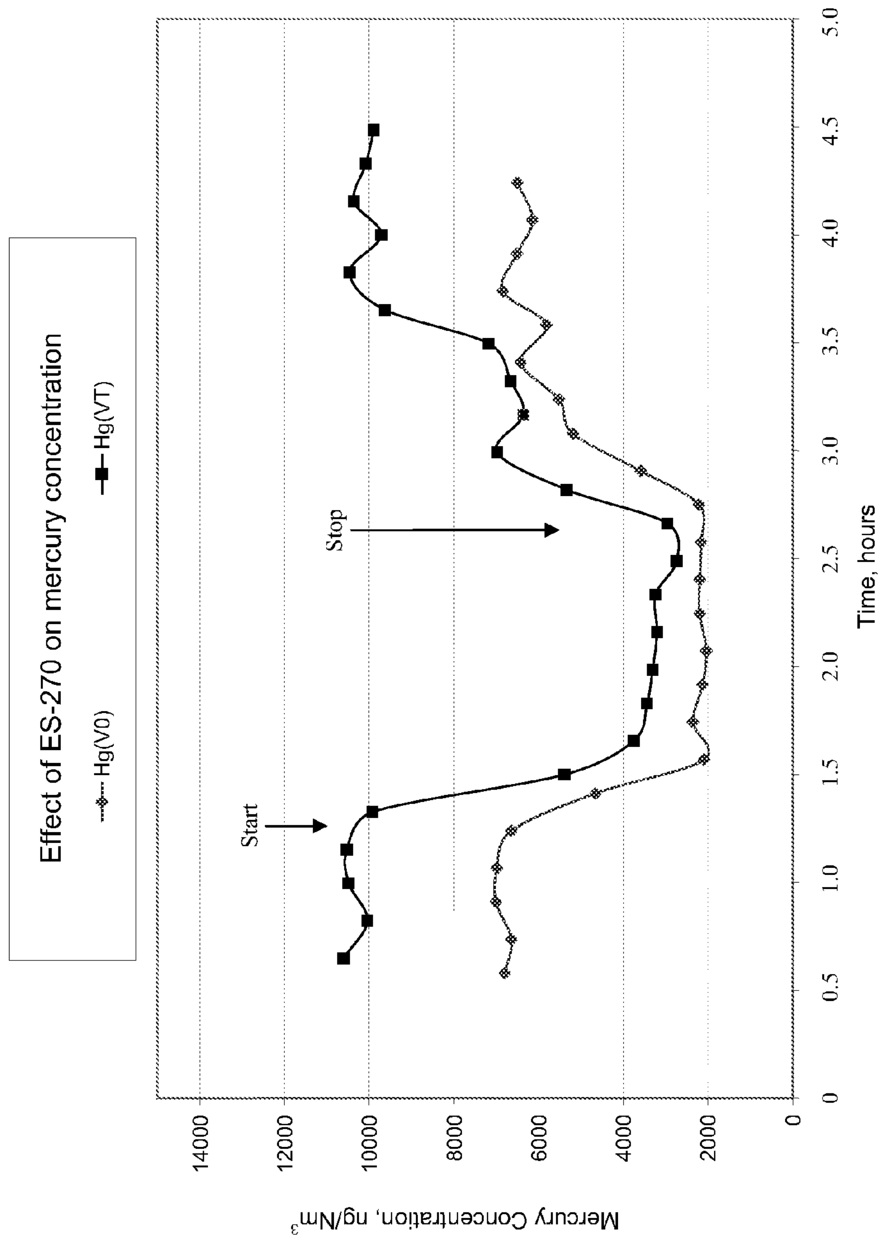

Effect of ES-270 on mercury concentration
Hg(V0)
Hg(VT)
Start
Stop
Mercury Concentration, ng/Nm3
14000
12000
10000
8000
6000
4000
2000
0
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
Time, hours

Fig. 1

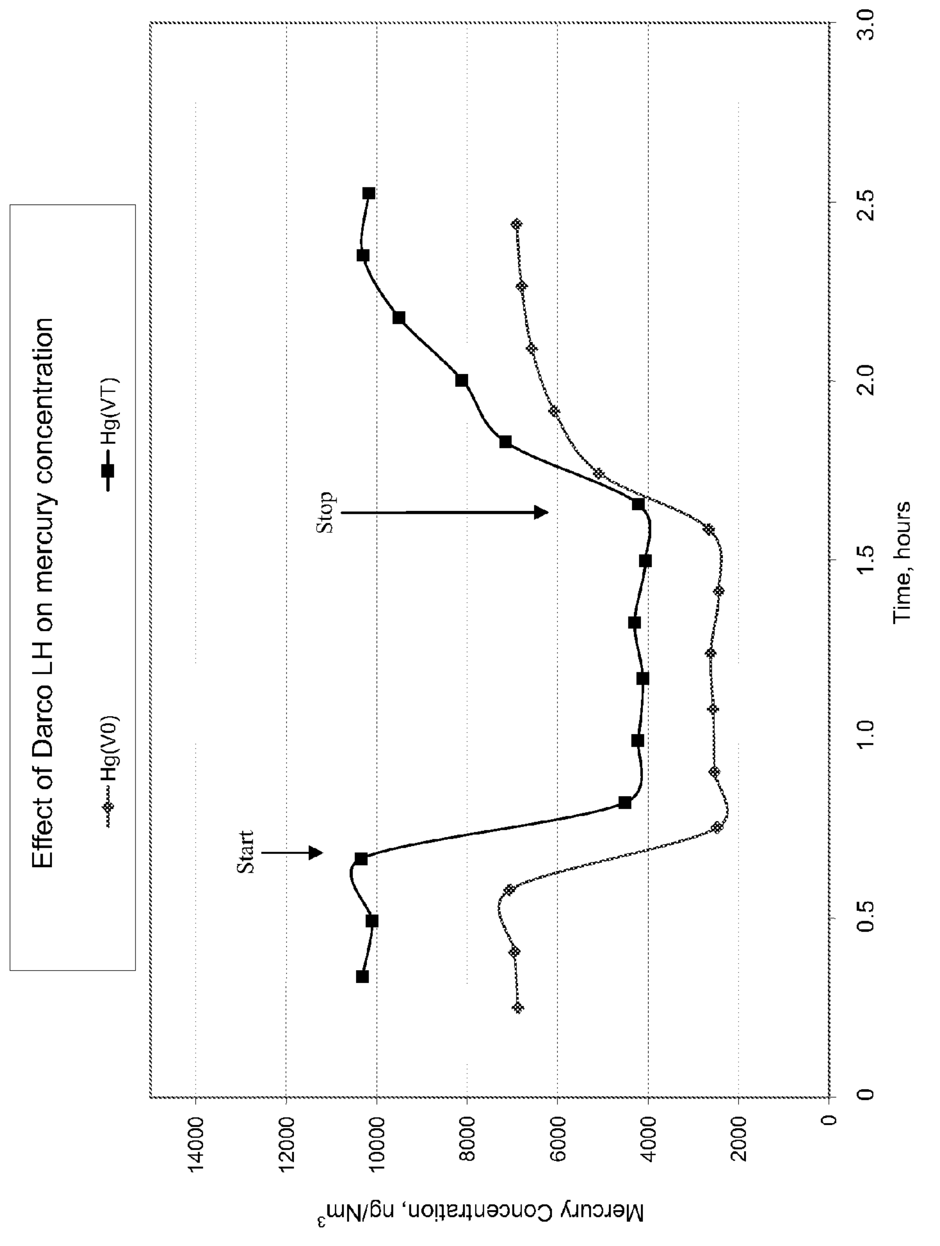

Effect of Darco LH on mercury concentration
Hg(V0)
Hg(VT)
Start
Stop
Mercury Concentration, ng/Nm3
Time, hours
0
2000
4000
6000
8000
10000
12000
14000
0.5
1.0
1.5
2.0
2.5
3.0

Fig. 2

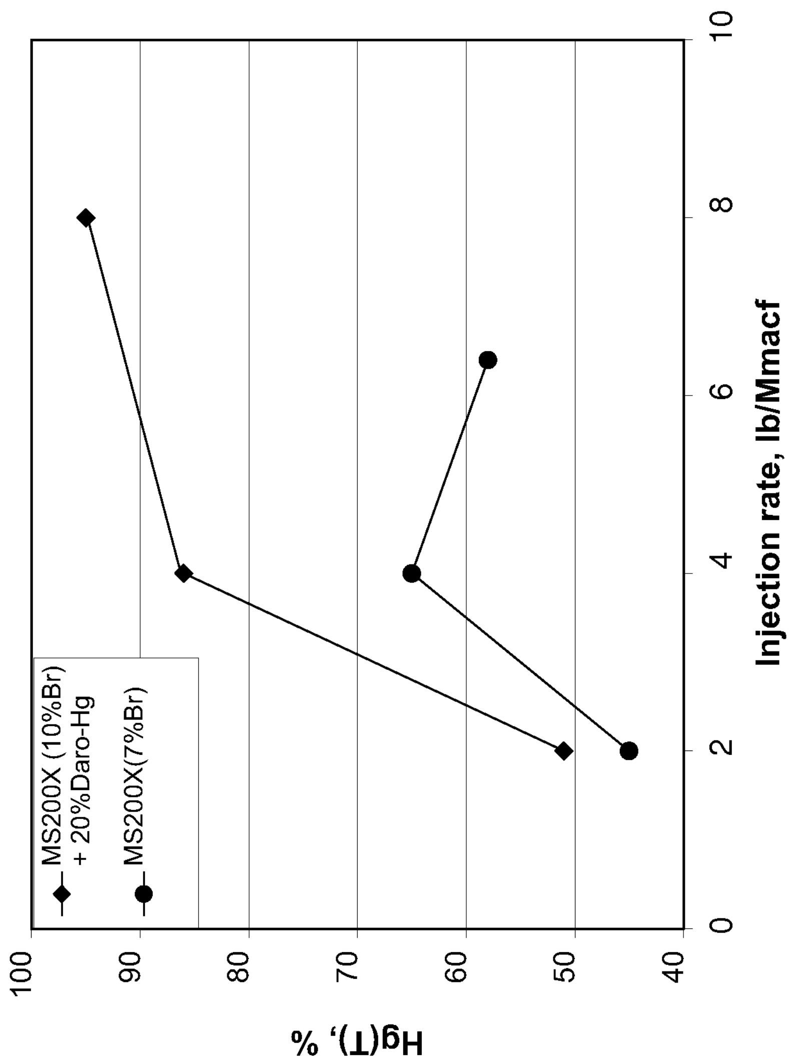

Hg(T), %
100
90
80
70
60
50
40
0
2
4
6
8
10
Injection rate, lb/Mmacf
MS200X (10%Br) + 20%Daro-Hg
MS200X(7%Br)

Fig. 3

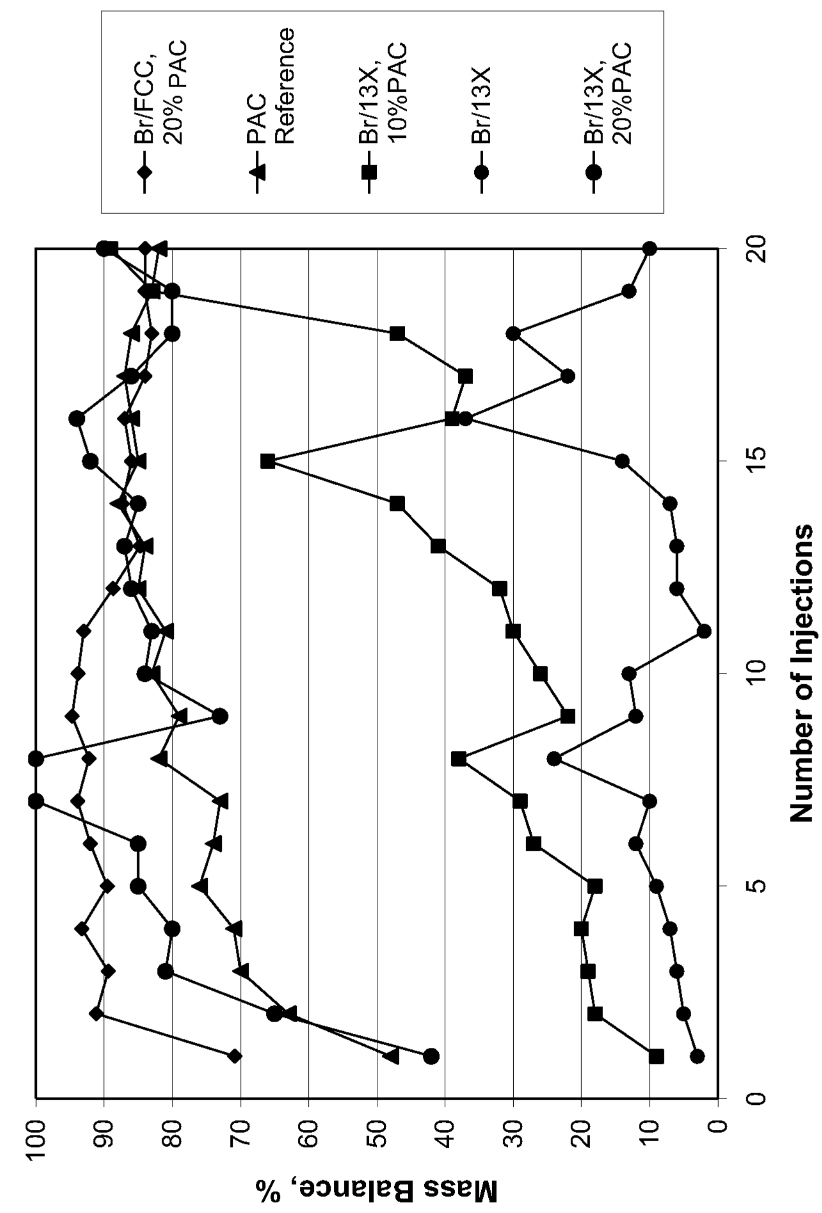

Mass Balance, %
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
Number of Injections
Br/FCC, 20% PAC
PAC Reference
Br/13X, 10%PAC
Br/13X
Br/13X, 20%PAC

Fig. 4

POLLUTANT EMISSION CONTROL SORBENTS AND METHODS OF MANUFACTURE AND USE

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation U.S. application Ser. No. 12/707,450, filed Feb. 17, 2010, which is continuation-in-part of U.S. application Ser. No. 12/329,246, filed Dec. 5, 2008, which is a continuation-in-part of U.S. application Ser. No. 11/860,148, filed Sep. 24, 2007, the contents of which are incorporated herein in their entirety.

TECHNICAL FIELD

Embodiments of the invention relate to sorbents for the removal of pollutants such as mercury from gas streams, methods for manufacturing sorbents and the use of sorbents in pollution control.

BACKGROUND

Emission of pollutants, for example, mercury, from combustion gas sources such as coal-fired and oil-fired boilers has become a major environmental concern. Mercury (Hg) is a potent neurotoxin that can affect human health at very low concentrations. The largest source of mercury emission in the United States is coal-fired electric power plants. Coal-fired power plants account for between one-third and one-half of total mercury emissions in the United States. Mercury is found predominantly in the vapor-phase in coal-fired boiler flue gas. Mercury can also be bound to fly ash in the flue gas.

On Dec. 15, 2003, the Environmental Protection Agency (EPA) proposed standards for emissions of mercury from coal-fired electric power plants, under the authority of Sections 111 and 112 of the Clean Air Act. In their first phase, the standards could require a 29% reduction in emissions by 2008 or 2010, depending on the regulatory option chosen by the government. In addition to EPA's regulatory effort, in the United States Congress, numerous bills recently have been introduced to regulate these emissions. A number of local and state governments have also passed or are considering passing stringent regulations to reduce mercury emissions, especially from power utility plants. These regulatory and legislative initiatives to reduce mercury emissions indicate a need for improvements in mercury emission technology.

There are three basic forms of Hg in the flue gas from a coal-fired electric utility boiler: elemental Hg (referred to herein by the symbol Hg^0); compounds of oxidized Hg (referred to herein the symbol Hg^{2+}); and particle-bound mercury. Oxidized mercury compounds in the flue gas from a coal-fired electric utility boiler may include mercury chloride ($HgCl_2$), mercury oxide (HgO), and mercury sulfate ($HgSO_4$). Oxidized mercury compounds are sometimes referred to collectively as ionic mercury. This is because, while oxidized mercury compounds may not exist as mercuric ions in the boiler flue gas, these compounds are measured as ionic mercury by the speciation test method used to measure oxidized Hg. The term speciation is used to denote the relative amounts of these three forms of Hg in the flue gas of the boiler. High temperatures generated by combustion in a coal boiler furnace vaporize Hg in the coal. The resulting gaseous Hg^0 exiting the furnace combustion zone can undergo subsequent oxidation in the flue gas by several mechanisms. The predominant oxidized Hg species in boiler flue gases is believed to be $HgCl_2$. Other possible oxidized species may include HgO, $HgSO_4$, and mercuric nitrate monohydrate ($Hg(NO_3)_2.H_2O$).

Gaseous Hg (both Hg^0 and Hg^{2+}) can be adsorbed by the solid particles in boiler flue gas. Adsorption refers to the phenomenon where a vapor molecule in a gas stream contacts the surface of a solid particle and is held there by attractive forces between the vapor molecule and the solid. Solid particles are present in all coal-fired electric utility boiler flue gas as a result of the ash that is generated during combustion of the coal. Ash that exits the furnace with the flue gas is called fly ash. Other types of solid particles, called sorbents, may be introduced into the flue gas stream (e.g., lime, powdered activated carbon) for pollutant emission control. Both types of particles may adsorb gaseous Hg in the boiler flue gas.

Sorbents used to capture mercury and other pollutants in flue gas are characterized by their physical and chemical properties. The most common physical characterization is surface area. The interior of certain sorbent particles are highly porous. The surface area of sorbents may be determined using the Brunauer, Emmett, and Teller (BET) method of N_2 adsorption. Surface areas of currently used sorbents range from 5 m^2/g for Ca-based sorbents to over 2000 m^2/g for highly porous activated carbons. EPA Report, Control of Mercury Emissions From Coal-Fired Electric Utility Boilers, Interim Report, EPA-600/R-01-109, April 2002. For most sorbents, mercury capture often increases with increasing surface area of the sorbent.

Mercury and other pollutants can be captured and removed from a flue gas stream by injection of a sorbent into the exhaust stream with subsequent collection in a particulate matter control device such as an electrostatic precipitator or a fabric filter. Adsorptive capture of Hg from flue gas is a complex process that involves many variables. These variables include the temperature and composition of the flue gas, the concentration and speciation of Hg in the exhaust stream, residence time, and the physical and chemical characteristics of the sorbent.

Currently, the most commonly used method for mercury emission reduction is the injection of powdered activated carbon (PAC) into the flue stream of coal-fired and oil-fired plants. Coal-fired combustion flue gas streams are of particular concern because their composition includes trace amounts of acid gases, including SO_2 and SO_3, NO and NO_2, and HCl. These acid gases have been shown to degrade the performance of activated carbon. Though powdered activated carbon (PAC) is somewhat effective to capture oxidized mercury species such as Hg^{2+}, PAC is not as effective for elemental mercury, which constitutes a major Hg species in flue gas, especially for subbituminous coals and lignite. The use of brominated powdered activated carbon (BPAC) is described in U.S. Pat. No. 6,953,494. According to U.S. Pat. No. 6,953,494, bromine species were introduced in PAC by a gas-phase process with Br_2 or HBr precursor in the vapor phase, both of which are highly toxic and a potential environmental hazard.

The coal-fired utility industry continues to seek new, cost-effective sorbents for controlling mercury emissions while also preserving the value of fly ash as a raw material for quality conscious applications. Evaluations of powdered activated carbon sorbents have shown consistent, adverse impacts on fly ash, a coal utilization by-product, sufficient to render it unusable in cement applications. These impacts include elevated residual carbon levels in the fly ash that exceed application specified limits, interference with the performance of air entrainment additives (AEA), which are used to improve the freeze-thaw properties and workability of cement, and cosmetic discoloration. Efforts are being made in the marketplace to minimize these impacts inherent to carbon based sorbents.

As noted above, alternatives to PAC or Br-PAC sorbents have been utilized to reduce mercury emissions from coal-fired boilers. Examples of sorbents that have been used for mercury removal include those disclosed in United States Patent Application Publication No. 2003/0103882 and in U.S. Pat. No. 6,719,828. In United States Patent Application Publication No. 2003/0103882, calcium carbonate and kaolin from paper mill waste sludge were calcined and used for Hg removal at high temperatures above 170° C., preferably 500° C. U.S. Pat. No. 6,719,828 teaches the preparation of layered sorbents such as clays with metal sulfide between the clay layers and methods for their preparation. The method used to prepare the layered sorbents is based on an ion exchange process, which limits the selection of substrates to only those having high ion exchange capacity. In addition, ion exchange is time-consuming and involves several wet process steps, which significantly impairs the reproducibility, performance, scalability, equipment requirements, and cost of the sorbent. For example, a sorbent made in accordance with the teachings of U.S. Pat. No. 6,719,828 involves swelling a clay in an acidified solution, introducing a metal salt solution to exchange metal ions between the layers of the clay, filtering the ion exchanged clay, re-dispersing the clay in solution, sulfidation of the clay by adding another sulfide solution, and finally the product is filtered and dried. Another shortcoming of the process disclosed in U.S. Pat. No. 6,719,828 is that the by-products of the ion exchange process, i.e., the waste solutions of metal ions and hydrogen sulfide generated from the acidic solution, are an environmental liability.

There is an ongoing need to provide improved pollution control sorbents and methods for their manufacture. It would be desirable to provide mineral-based sorbents containing bromine on the sorbent substrate that can be manufactured easily and inexpensively, do not impair the value of fly ash or pose environmental concerns. Furthermore, simple and environmentally friendly methods that effectively disperse bromine on readily available mineral substrates are needed

SUMMARY

Aspects of the invention include compositions, methods of manufacture, and systems and methods for removal of heavy metals and other pollutants from gas streams. In particular, the compositions and systems are useful for, but not limited to, the removal of mercury from flue gas streams generated by the combustion of coal. One aspect of the present invention relates to a sorbent made by a method comprising dispersing a bromide salt on a mineral sorbent substrate by impregnating powdered mineral substrate particles with a bromide salt solution followed by drying or by spray-drying a mixture slurry of a bromide salt and a mineral sorbent substrate. In one embodiment, the method optionally includes reducing the particle size of the sorbent particles. Another aspect of the invention pertains to sorbents that include dispersing of a bromide on a sorbent that has low surface area, which significantly improves Hg-capture. Yet another aspect of the present invention provides sorbents and methods to enhance the properties of concrete by adding fly ash that contain injected brominated mineral sorbents.

One or more embodiments pertain to a sorbent comprising bromine-containing species dispersed on mineral substrate particles, the mineral substrate having a total carbon content less than about 10 weight percent, the sorbent being adapted for removing mercury from a combustion flue gas in an exhaust gas system. In one or more embodiments, the carbon content of the particles is less than about 3 weight percent. In other embodiments, the oxidative sorbent compositions contain activated carbon in an amount up to 30% by weight.

One or more embodiments of this invention pertain to a method for making mineral sorbents for mercury capture comprising physical blending of the sorbent particles with a second particle component which is a flow modifier, such as a powdered activated carbon, to effectively reduce the agglomeration of the mineral sorbent particles and significantly increase its mercury capture efficiency. The amount of second particle component (i.e., flow modifier) added is such that it should reduce the agglomeration of the mineral sorbent particles and preferably not affect the compatibility of the sorbent composition with cement for concrete applications.

According to embodiments of the invention, the mineral substrate particles comprise materials selected from the group consisting of alumina, silica, titania, zirconia, iron oxides, zinc oxide, rare earth oxides, metal carbonate, metal sulfate, aluminosilicates, zeolites, clays such as kaolin, bentonite or attapulgite, heat-treated clays, chemical-surface modified clays, talc, fly ash, fluid cracking catalyst particles, dirt, and combinations thereof. When zeolites are used, a particularly useful zeolite is 13X.

In one or more embodiments, the bromine species includes a salt selected from the group consisting of sodium bromide, ammonium bromide, hydrogen bromide, potassium bromide, lithium bromide, magnesium bromide, calcium bromide, beryllium, zinc bromide, metal bromide and organic bromide that can release bromide or bromate ions and combinations thereof. According to one or more embodiments, the particles have a bromine content in the range of about 0.1 weight percent and 20 weight percent. In other embodiments, the oxidatively active halide is not limited to bromide, but includes iodide and chloride as well. By "oxidatively active" is meant that the halide is a halide of a nonoxidative, alkaline metal cation, such as sodium, potassium, or alkaline earth metal cations, such as calcium or magnesium. The halide can be also a halide of a transition metal cation such as zinc. While not wishing to be bound by a particular theory, it is believed that when used in the oxidative sorbent compositions of the present invention, the oxidatively active halides either act as a surface for mercury to bind and become oxidized by oxygen in the fluid stream, or first themselves become oxidized by oxygen in the fluid stream, which can function to oxidize elemental mercury.

In a specific embodiment, the particles are selected from the group consisting of kaolin, FCC fines, and combinations thereof. In another specific embodiment, the particles comprise as-mined kaolin without any beneficiation. In another embodiment, the bromide salt is uniformly dispersed on the surface of the kaolin particles.

In one or more embodiments, a flow modifier is physically blended with the brominated mineral sorbent to reduce agglomeration and improve flow characteristics of the mineral sorbents. The amount of the flow modifier added is up to 30 wt % of the total blend. The flow modifier can be a powder activated carbon or a halogenated activated carbon. The flow modifier can be also mineral particles including particles of heat-treated clay, surface-treated clay, silica, alumina, pseudo boehmite, FCC particles, and fly ash.

In a specific embodiment, the flow modifier is typically a material which, when physically blended with the mineral sorbent substrate, produces a composition which improves the mass balance as compared to the mineral sorbent substrate alone when measured by acoustically driven aerosol injection methods such as described in more detail below. In one embodiment of the invention the number of injections to obtain a mass balance of greater than or equal to those of activated carbon.

In another specific embodiment, the flow modifier is typically a material which, when physically blended with the mineral sorbent substrate, produces a composition which increases the overall mercury capture rate by more than 10% as compared to mineral sorbent alone.

Another aspect pertains to a method of making brominated mineral sorbent for the removal of mercury from a combustion gas in an exhaust gas system comprising dispersing a bromide salt in a solid or liquid phase onto mineral sorbent substrate particles, the mineral sorbent substrate particles containing less than about 10 weight percent carbon. In certain embodiments, the carbon content is less than about 3 weight percent. Typically, the carbon is in the form of impurities, that is, carbon that has not been added to the sorbent. However, it is within the scope of the invention to add carbon, for example, by mixing the sorbent with an organic bromide such as methyl bromide. The substrates and salts can be those listed immediately above, according to one or more embodiments. The method may further comprise drying the particles having the bromide salt dispersed thereon at a temperature in the range of about 25° C. and about 200° C. The bromide may have a loading level in the range of about 0.1 to about 20 weight percent, and in specific embodiments, in the range of about of about 3 to about 15 weight percent. The method may further comprise blending the brominated sorbent particles with a flow modifier. The amount of the flow modifier is in the amount of up to 30 wt % of the total blend.

Another aspect pertains to a method of blending cement with fly ash that contains the brominated mineral sorbents. The concentration of the brominated mineral sorbent in fly ash is in the range of 0.01 to 20%.

The method may further include reducing the sorbent particle size to an average particle size of less than about 100 μm, and in specific embodiments, less than about 20 μm. In specific embodiments, the sorbent particles comprise FCC fines, and the FCC fines comprise Y-zeolite in Na form. In one or more embodiments, the sorbent particles comprise mixture of brominated kaolin and brominated FCC fines. In other embodiments, the sorbent particles comprise mixture of brominated fly ash and brominated FCC fines. In other embodiments, the particles comprise mixture of brominated kaolin and one or more mineral substrate. In other embodiments, the sorbent particles comprise mixture of brominated fly ash and one or more mineral substrates. In other embodiments, the particles comprise mixture of brominated FCC fines and one or more mineral substrates.

Another aspect pertains to a method of removing mercury from a combustion gas in an exhaust gas system comprising injecting a physical blend of brominated sorbent particles and flow modifier particles, the blend particle system being adapted for removing mercury from a combustion gas in an exhaust gas system. The brominated sorbent particles are selected from the group consisting of alumina, silica, titania, zirconia, iron oxides, zinc oxide, rare earth oxides, metal carbonate, metal sulfate, aluminosilicates, zeolites, heat-treated clays, chemical-surface modified clays, fly ash, fluid cracking catalyst particles, dirt, and combinations thereof. The flow modifiers are selected from the group consisting powdered activated carbon, brominated powdered activated carbon, heat-treated clay, chemical-treated clay, silica, alumina, pseudo boehmite, fly ash, and FCC particles. In certain embodiments, the sorbent particles comprise a spray-dried mixture of zeolite and a bromine salt.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a graph showing an ion-flight mercury capture profile of a brominated kaolin sorbent in a drop-tube reactor;

FIG. **2** is a comparative in-flight mercury profile of Br-PAC under the same testing conditions as for the data in FIG. **1**;

FIG. **3** is a graph showing the total mercury capture of a brominated 13X zeolite sorbent at 2 second residence time with and without the addition of activated carbon at different injection rate; and

FIG. **4** is a graph showing the mass balance of brominated 13X zeolite and brominated FCC fines compositions with and without blending of an activated carbon flow modifier.

DETAILED DESCRIPTION

Before describing several exemplary embodiments of the invention, it is to be understood that the invention is not limited to the details of construction or process steps set forth in the following description. The invention is capable of other embodiments and of being practiced or being carried out in various ways.

As used in this specification and the appended claims, the singular forms “a”, “an” and “the” include plural referents unless the context clearly indicates otherwise. Thus, for example, reference to “a sorbent” includes a mixture of two or more sorbents, and the like.

Aspects of the invention provide improved sorbents, which may be used to remove mercury and other pollutants from the combustion gases, for example, flue gases of coal-fired and oil-fired boilers, methods for manufacturing such sorbents, and systems and methods utilizing these sorbents. The sorbents comprise brominated substrates in the form of particles having a carbon content of less than about 10 weight percent. A wide variety of substrates, regardless of their porosity, purity, or ion exchange capacity, can be manufactured and used for mercury removal in accordance with the present invention. As used herein, the term substrate refers to the material onto which a bromide salt is dispersed and pollutant is then adsorbed in a pollution removal system.

Suitable substrate sorbent materials in accordance with embodiments of the present invention include any inorganic or organic materials that are stable under the flue gas conditions (temperature, pressure, gas components, residence time, etc). The sorbents according to one or more embodiments comprise particles having carbon content of less than about 10 weight percent, and in specific embodiments, less than about 3 weight percent. Suitable sorbents include, but are not limited to, commonly used oxides such as alumina, silica, titania, zirconia, iron oxides, zinc oxide, rare earth oxides, metal carbonate, metal sulfate, aluminosilicates, zeolites, kaolin, metakaolin, fully calcined kaolin, talc, bentonite, attapulgite, talc, coal boiler fly ash, common dirt, fluid cracking catalyst (FCC) particles, etc.

In specific embodiments, especially useful particles comprise as-mined kaolin. As-mined kaolin refers to kaolin that has been mined and not beneficiated or calcined. In another specific embodiment, especially useful sorbent particles comprise fluid cracking catalyst particles. In other specific embodiments, the sorbent particles comprise fly ash particles. In addition to having favorable properties, these mineral substrates are also cost-effective and environmentally friendly.

Kaolin, also known as kaolinite or hydrous kaolin, is a common clay mineral. Kaolin contains mainly silicon and aluminum in a layered aluminosilicate structure. Kaolin is extensively used for coating, functional filler, ceramics additive and many other applications because of its fine particles size, white color, and inertness, among other chemical and physical properties. Its low cost is also a key factor for its widespread use. Kaolin is also a very important raw material for many industries such as concrete, catalysis, and paper coating after high temperature or chemical treatment. There are small amount of impurities in kaolin, depending on the location of the deposit. For many applications, the impurities in as-mined kaolin, such as TiO_2, Fe_2O_3, and organic materials or carbonaceous matter, need to be removed, which is known as clay beneficiation. We found that, although kaolin has a low BET surface area, typically 10-30 m^2/g, it leads to a surprisingly high mercury capture performance when it is used as a low cost mineral substrate for our brominated sorbents. Furthermore, impurities in as-mined kaolin, such as the organic or carbonaceous materials, actually enhance the overall mercury capture efficiency of the brominated sorbent possibly due to the increase of bonding of bromine species to the substrate and decrease of kaolin's density, stickiness, and water adsorption.

Fly ash is the by-product of coal combustion. After experiencing high temperature combustion in boiler, fly ash has a bulk chemical composition of aluminosilicate and other inorganic oxides such CaO, MgO, Fe_2O_3, and TiO_2, depending on the coal source and rank. PRB and sub-bituminous coals have high concentration of CaO in their fly ash. Under electron microscope, fly ash has a morphology of irregular beads or broken beads. The surface area of fly ash is very low, BET surface area below 5 m^2/g. It was found that residual unburnt carbon in fly ash can increase the ionic mercury capture. We found that fly ashes, regardless of their coal sources, are all excellent low cost mineral substrate for our brominated sorbents.

FCC particles may be obtained from the end stage or intermediate stage of an FCC particle manufacturing process, or alternatively, they may be generated during a fluid catalytic cracking process that uses FCC particles and generates FCC fine particles. In particular embodiments, the methods and systems utilize fluid cracking catalyst fine particles, which will be interchangeably referred to as "FCC fines" or "FCC fine particles". The fluid cracking catalyst fine particles may be recovered and separated from a fluid cracking catalyst manufacturing process or recovered and separated from a fluid catalytic cracking process that uses FCC particles and generates FCC fines. In specific embodiments, zeolite-containing FCC fines and intermediate FCC fines are provided as sorbents for the removal of mercury from gas streams.

The terms "fluid cracking catalyst fines" or "FCC fines" are used herein to refer to fine solid particles obtained from a fluid cracking catalyst manufacturing process, such as described in, but not limited to U.S. Pat. Nos. 6,656,347 and 6,673,235, and to particles generated and separated during a fluid catalytic cracking process that uses FCC particles. For particles formed during a fluid catalytic cracking particles manufacturing process, the particles may be separated during one or more intermediate stages of the manufacturing process, or at an end stage. A good fluid cracking catalyst requires the particle size above 40 microns. During the production of these FCC catalysts, a large volume of fine particles in the range of about 0 to 40 um in excess of that required for good fluidization in the refinery are often generated. Heretofore, a suitable use for these excess fine particles has not been found, and so they are therefore land-filled, which incurs cost for the plants. The disposal of the FCC waste by-products, referred as FCC fines, has been a long-standing concern for FCC manufacturing.

Depending on at which stage the FCC fines are collected, the main composition of the particles include zeolite (mostly Y-zeolite in sodium form), kaolin, metakaolin, sodium silicates, silica, and alumina. Thus, the chemical and physical characteristics can be varied considerably based on the FCC production process and post treatment. FCC fines have a BET surface area in the range between 200 to 600 m^2/g. The surface area of as-collected FCC fines can be further increased by washing. Heating treatment could also alter the surface area and surface chemical properties of FCC fines particles. Composition, porosity, and particle size can all impact the mercury capture when FCC fines are used as a mercury capture sorbent by itself or as the substrate for the brominated sorbent. The most economical and readily available FCC fines are those collected during the production of Na—Y zeolite. The fines are collected by a filter as a wet cake which can be then dried and ground or spray-dried. Thus, the use of FCC fines in manufacturing a mercury removal injection sorbent described herein not only provides an economical mineral substrate, but also helps solve the FCC waste disposal issue. Furthermore, FCC fines alone have useful ionic mercury capture capacity, as described in commonly-assigned United States Patent Application Publication No. 2007/0289447 A1, dated Dec. 20, 2007, and entitled, Methods and Manufacturing Mercury Sorbents and Removing Mercury From a Gas Stream. Thus, when used as the substrate for the brominated sorbent or physically blended with a brominated sorbent, FCC fines helps increase the mercury capture efficiency especially ionic mercury.

The sorbent particles according to one or more embodiments of the invention comprise a single-component brominated material. According to other embodiments, the sorbent is a mixture of two or more brominated materials, for example a mixture of brominated kaolin and brominated FCC fines. According to another embodiment, the sorbent comprises a brominated mixture of two or more substrates such as fly ash and FCC fines. Yet according to another embodiment, the sorbent is a mixture of brominated sorbent and a bromine-free substrate, for example a mixture of brominated kaolin and FCC fines.

For a porous brominated sorbent, elemental mercury is oxidized into ionic form due to the bromide, and the ionic mercury is stored inside the pores of the support. Pure zeolites have more cation-exchangeable sites, higher porosity, and thus higher mercury storage capacity than FCC fines, kaolin, or fly ash, though the cost of a pure zolite is usually high. Most commonly used zeolites include aluminosilicate zeolites such A, X, Y, ZSM-5, Beta, chabazite, and titanosilicate zeolites such as ETS-10. Among all the brominated zeolites we have tested, those zeolites, such as 13X, which have the lowest Si/Al ratio, highest surface area and pore volume, and largest pore size gives the highest mercury capture.

One of the major obstacles in using a mineral sorbent for capturing mercury in the flue gas is the agglomeration of sorbent particles. This is largely due to the strong interactions (stickiness) among mineral particles as compared to, for example, a powdered activated carbon. The agglomeration of sorbent particles greatly hinders sorbent flow ability and its dispersion in the flue gas (i.e., the effective collision with the mercury species in flue gas), and thus reduces its mercury capture efficiency. This invention shows that a physical blending of the sorbent particles with a second particle component, such as a powdered activated carbon, can effectively reduce the agglomeration of the mineral sorbent particles and significantly increase their mercury capture efficiency. The amount of second particle component (i.e., flow modifier) added is such that it should reduce the agglomeration of the mineral sorbent particles and preferably not affect compatibility of the sorbent composition with cement for concrete applications.

As used herein, the term "flow modifier" refers to any material that reduces agglomeration of the particles of the mineral substrate of the invention. Such flow modifiers are known in the art for reducing or preventing clumping of solid particles such that they are "fluidized" and therefore tend to move as discrete particles which resemble a free flow fluid rather than as chunks or agglomerated clumps. By reducing or preventing agglomeration of solid particles by use of a flow modifier, processing and handling of such materials is simplified and manufacturing processes are more consistent. Flow modifiers useful in the invention may also be referred to as "powder flow modifiers," "solid flow modifiers," or "flowing agents." A flow modifier useful in the invention is typically a material which, when physically blended with the mineral sorbent substrate, produces a composition which improves the mass balance as compared to the mineral sorbent substrate alone when measured by acoustically driven aerosol injection methods such as described in more detail below. In one embodiment of the invention the blended sorbent composition obtains a mass balance greater than or equal to that of powdered activated carbon with 1-6 injections at 0% humidity as compared to a maximum achievable mass balance of about 40% or less for the mineral sorbent substrate alone. In further embodiments the blended sorbent composition obtains a mass balance greater than or equal to that of powdered activated carbon with 2-6 injections, 3-5 injections or 3-4 injections at 0% humidity. In specific embodiments, the blended sorbent compositions obtain a mass balance of equal to or greater than 70% after 1-6 injections or a mass balance of equal to or greater than 80% after 3-5 injections at 0% humidity.

Loading

The substrate particles according to one or more embodiments are brominated. In specific embodiments, bromide salts are dispersed on substrate. Non-limiting examples of the bromide salts include sodium bromide, ammonium bromide, hydrogen bromide, potassium bromide, lithium bromide, magnesium bromide, calcium bromide, beryllium bromide, zinc bromide, other metal bromides, and organic bromides that can release bromide or bromate ions and combinations thereof.

The loading level of bromide is up to about 50% by weight. In specific embodiments, the loading is in the range of about 0.1% by weight to about 20% by weight. In a more specific embodiment, the bromine loading is in the range of about 3% by weight to about 15% by weight.

The bromide salts can be dispersed on the surface of the sorbent particles using any method so long as the bromide salt is well dispersed on the surface of the substrate. Some bromine species may get into the pores of the substrates such as Y-zeolite in FCC fines. Suitable dispersion methods include, but are not limited to, impregnation (incipient wetness), solid-state mixing, spray-drying, sprinkling of solution on the substrate, precipitation, and/or co-precipitation. If a solvent is required to disperse the bromide salt, it can be water or an organic solvent. Non-limiting examples of organic solvents are acetone and alcohol.

In a specific embodiment, the sorbent particles comprise about 0.1 to about 10 weight % Br on kaolin or a fly ash. Kaolin and fly ash substrate particles require less bromide salt than other particles that have been investigated to provide an effective sorbent. Also, it is believed that compared to other particles investigated, kaolin and fly ash have less moisture sensitivity. Kaolin also has the desirable property that kaolin particles can be reduced to a smaller sorbent particle size and it has a lower bulk density than fly ash. Although the present invention should not be not bound by any theory, it is believed that the low surface area of kaolin and fly ash allows most of the bromide to be concentrated on the particle surface and thus have a better chance to interact with mercury pollutant species during the short residence time of the sorbent particles in the flue gas.

As noted above, the sorbent particles contain less than 10 weight percent carbon, and in particular embodiments, less than 3 weight percent carbon. Natural impurities in kaolin, such as intercalated organic or carbonaceous species, or the unburned carbon in fly ash may have a positive impact on the sorbent performance as the impurities can modify the sorbent bulk density, surface hydrophobicity, and bonding strength with bromine species.

Large scale sorbent production can be achieved by a spray-drying process which involves dissolving bromide salt in water first, adding mineral substrate to the solution, and then spray-drying the slurry in a standard industrial spray drier. In another embodiment, aqueous solution of bromide salt can be added to a mineral substrate-water slurry before spray drying.

Blending

The blending of the powdered halogenated mineral sorbent with a powdered flow modifier is done by a simple physical mixing. The mixing step can be accomplished by adding the flow modifier particles continuously as the spray dried sorbent particles exit from the spray drier. It can be also achieved batch-wise by contacting the two particle types and stirring for a sufficient amount of time for mixing. The final blended product should have a uniform composition and will have a grayish appearance if carbon is used as a flow modifier.

Without intending to limit the invention in any manner, the present invention will be more fully described by the following examples.

EXAMPLES

Examples 1-15

Sorbent Preparation by Impregnation

The general procedures of making a brominated mineral sorbent according to one or more embodiments include (1) dissolving a bromide salt in water; (2) impregnating the solution to the mineral substrate powder using the standard incipient wetness method; and (3) drying the wet solid either at room temperature by vacuum or at a temperature between 100° C. and 200° C., and (4) grinding the dried solid to a particle size below 325 mesh.

Table 1 lists the main ingredients of selected examples of brominated mineral sorbents prepared based on the above procedures using different mineral substrates.

TABLE 1

Selected Brominated Mineral Sorbent Preparations

Example	Substrate	$W_{substrate}$ (g)	Br Salt	$W_{Br\ Salt}$ (g)	H_2O (g)
1	FCC fines	23.0	NaBr	3.53	9.6
2	FCC fines	12.5	NH_4Br	1.56	7.2
3	$CaCO_3$	10.5	NaBr	1.76	2.5
4	(50% FCC fines + 50% CaCO3)	11.5 + 10.5	NaBr	3.5	12
5	Fly ash	20.0	NaBr	1.65	2.4

TABLE 1-continued

Selected Brominated Mineral Sorbent Preparations

Example	Substrate	$W_{substrate}$ (g)	Br Salt	$W_{Br\ Salt}$ (g)	H_2O (g)
6	ATH	22.0	NaBr	1.65	13.7
7	Metamax	22.0	NaBr	1.65	16.2
8	Kaolin-1	22.0	NaBr	1.65	7.7
9	Kaolin-2	22.0	NaBr	1.65	6.0
10	Kaolin-3	22.0	NaBr	1.65	5.2
11	Kaolin-1	22.0	$CaBr_2$	1.74	8.3
12	Kaolin-1	22.0	HBr	4.7	4.6
13	Kaolin-1	22.0	HBr	2.6	6.4
14	FCC fines	—	—	—	—
15	Kaolin-1	—	—	—	—

In table 1, three kaolin samples, -1, -2, and -3, were obtained from BASF without further treatment. Kaolin-1 is an as-mined kaolin containing about 2% naturally intercalated carbon. It has a grayish color. Kaolin-2 is another as-mined sample, containing less than 1% organic matter and having a beige color. Kaolin-3 is a beneficiated sample from Kaolin-2. FCC fines particles were obtained by drying the FCC fines wet cake (obtained from BASF FCC manufacturing plants) at 105° C. overnight followed by grinding or by spray-drying the slurried wet cake in water. Fly ash was obtained from the baghouse of a power plant. Metamax is a BASF metakaolin product which was obtained by heat treatment of kaolin. ATH is an alumina trihydrate product from Chalco in China. $CaCO_3$ (98%) was from Aldrich. HBr (48% aqueous solution), NaBr (99%), and NH_4Br (99%) were all from Alfa Aesar.

Examples 16-17

Sorbent Preparation by Spray Drying

To make the spray-dried samples, the general procedure comprises dissolving bromide in water first, adding mineral substrate in the solution and stir to make a uniform slurry that is suitable for spray-drying in a standard spray drier. Spray-drying outlet temperature is 120° C.-160° C., typically 120° C. The spray drier outlet pressure and nozzles size are chosen in such that the final sorbent particle size is within the required range. Table 2 lists the main ingredients of two spray-dried samples made by two different spray driers.

TABLE 2

Selected Brominated Mineral Sorbent Preparations by spray drying

Example	Substrate	$W_{substrate}$ (kg)	Br Salt	$W_{Br\ Salt}$ (kg)	H_2O (kg)	Spray-drier
16	FCC fines wet cake	1.57	NaBr	0.153	3.35	#1
17	Kaolin-1 powder	159	NaBr	11.8	409	#2

Example 18

Mercury Capture Efficiency Measurement

The mercury capture efficiency was measured by an outside commercial lab (ICSET of Western Kentucky University) with a drop-tube in-flight reactor. The mercury capture efficiency (%) is defined by Equation 1.

$$100\times[Hg(inlet)-Hg(outlet)]/[Hg(inlet)] \quad (1)$$

The total mercury is the sum of the ionic and atomic mercury species as illustrated in Equation 2.

$$Hg_{total}=Hg^0+Hg^{2+} \quad (2)$$

The drop-tube reactor of ICSET was installed at a commercial power plant. The carrier gas was the actual flue gas duct-piped from the boiler. The mercury in the actual flue gas has a distribution of about 70% elemental mercury and 30% ionic mercury. The sorbent was injected into the reactor after being mixed with a fly ash in a ratio of 1:250. The fly ash served as a diluent to help inject the sorbent. The sorbent residence time in the reactor is one second and the sorbent injection rate is typically 4 lb/MMacf. The measurement was performed at about 150° C. Table 3 lists the mercury capture efficiencies measured by ICSET. For comparison, two reference materials are also listed: Darco Hg-LH from Norit and pure fly ash.

TABLE 3

ICSET Mercury Capture Efficiency

Sample	Sorbent	Bromide	Injection rate lb/MMacf	Capture Efficiency (%) Hg_{Total}	Capture Efficiency (%) Hg^0
Reference	Darco Hg-LH	—	4	55	64
Reference	Darco Hg-LH	—	8	78	85
Reference	Pure fly ash	—	4	13	15
Example 1	12% Br/FCC fines	NaBr	4	46	42
Example 2	12% Br/FCC fines	NH_4Br	4	37	38
Example 3	12% Br/CaO_3f	NaBr	4	52	49
Example 4	12% Br/(CaCO3 + FCC fines)	NaBr	4	44	48
Example 5	6% Br/Fly ash	NH_4Br	4	41	31
Example 6	6% Br/ATH	NaBr	8	57	71
Example 7	6% Br/Metamax	NaBr	8	63	72
Example 8	6% Br/Kaolin-1	NnBr	4	52	54
Example 9	6% Br/Kaolin-2	NaBr	4	40	47
Example 10	6% Br/Kaolin-3	NaBr	4	35	46
Example 11	6% Br/Kaolin-1	CaBr2	4	52	60
Example 12	6% Br/Kaolin-1	HBr	4	41	37
Example 13	11% Br/Kaolin-1	HBr	4	54	68
Example 14	FCC fines	—	4	26	27
Example 15	Kaolin-1	—	4	27	32
Example 16	12% Br/fly ash	NaBr	4	41	47
Example 17	6% Br/kaolin-1	NaBr	4	69	66

FIG. **1** shows an in-flight mercury capture profile of a brominated kaolin sorbent in a drop-tube reactor. Note that the mercury concentration drops and recovers after the sorbent injection is started and stopped. FIG. **2** shows a comparative in-flight mercury profile of Norit Darco Hg-LH under the same testing conditions as for the data in FIG. **1**. The in-flight data shows that the brominated mineral sorbent has very similar mercury capture rate (drop slope) and capture efficiency (drop depth) for both elemental mercury Hg(V0) and total mercury Hg(VT) as the comparative carbon reference.

Example 19

Mercury Leachability and Cement Application

Mercury leachability is an important property for any injection sorbent due to the environmental concern of their long-term stability after exposure to the nature elements. The brominated mineral sorbents disclosed herein were tested for mercury leachability at IC SET using the standard Toxicity Characteristic Leaching Procedure (TCLP) method. The results showed that the mercury leachability of all the brominated sorbents tested is well below the universal treatment standard value of 25 ppb. The brominated mineral sorbents were also evaluated for their use, after mixing with fly ash, as additives in cement and concrete. Adding fly ash in cement reduces the overall usage of cement, which not only reduces the cost but also finds value for fly ash, a waste by-product of coal combustion. However, there are limits how much the fly ash can be added in the cement so that the properties of the final concrete properties will not be compromised. For example, ASTM C618 requires that the amount of fly ash in concrete should be limited in such that the water used in making concrete should be less than 105% as compared to the control that is without fly ash, the strength activity index (SAI) of concrete after 7 days should be higher than 75% of the control, and the fineness (the particles retained on a 45 μm sieve) should be below 34% while the foam index (number of drops) should be stable and below 20-30.

Table 4 lists the concrete formulations and testing results using cements that contain fly ash or fly ash plus a brominated kaolin sorbent. The data shows that adding 20% of fly ash to cement does not impair the properties of cement and concrete in general. The data also shows that, after adding 5 and 10% by weight brominated kaolin sorbent in the fly ash, the concrete strength activity index is noticeably increased while other properties remain the same. It is clearly indicated that the brominated mineral sorbents disclosed herein do not impair the use of fly ash for cement and concrete application. On the other hand, in some cases, the presence of the brominated mineral sorbents actually enhances the properties of cement and concrete.

TABLE 4

Cement and Concrete Formulation and Testing Results

	Control	Fly ash control	Br/kaolin ~2 lbs injection	Br/kaolin ~4 lbs injection
Formulation				
Cement	500	400	400	400
Sand	1375	1375	1375	1375
Fly Ash	0	100	95	90
6% Br/kaolin (Example 17)	0	0	5	10
W/CM/Water Water Requirement	.484/242 g	.440/220	.460/230	.460/230
W/CM/Water	.484/242 g	.440/220	.460/230	.460/230
Water Requirement	—	91	95	95
Strength Activity 7 Day				
Compressive PSI	4500	3680	4010	4060
SAI	—	82	89	90
Cube Density g/cc	2.21	2.22	2.23	2.23
Fineness				
Retained on 45 μ sieve %	—	21.6	22.4	22.5
Passing 45 μ sieve % (Fineness)	—	78.4	77.6	77.5
Foam Index Testing				
Number of Drops	5/5/5	9/10/9	9/9/9	10/9/9

Example 20

Blended Sorbent Preparation

In one embodiment, the general procedure for making the halogenated mineral sorbent comprises dissolving the halogen salt in water first, adding mineral substrate in the solution, stirring to make a uniform slurry, and spray-drying the slurry to form the final sorbent particles. Typical spray drier outlet temperature is 120-160° C. The spray drier outlet pressure and nozzles size or spinning wheel rate are chosen in such that the final sorbent particle size is within the required range.

The second particle component, which serves as a powder flow modifier, is then physically added to and mixed well with the halogenated mineral sorbent particles. The blended powder mixture may then be packaged and shipped. In one example, a flow modifier is powdered activated carbon (PAC) in an amount of 10-20 wt % of the total blended product.

Brominated oxidative sorbent compositions were prepared by the spray-drying method described above. Briefly, bromide salt was first dissolved in water, and 13X zeolite obtained from Sigma-Aldrich was then added to the solution while stirring. The total solid level in the slurry was about 30-40%. All the spray drying work was carried out in a small Niro spray drier. The brominated 13X zeolite powder was physically blended with a commercial activated carbon obtained from Norit, Darco-Hg®, which contains no bromine.

Example 21

Apogee Field Testing

Mercury slipstream in-flight capture testing was conducted by Apogee Scientific, Inc. at a utility power plant burning PRB coals. Mercury in-flight capture was conducted in a similar manner as those described above at ICSET except a pure sorbent powder was injected into the flue gas without using any fly ash diluent. Mercury concentration was recorded at 2 and 4 seconds of residence time at outlet ports and compared to the inlet mercury concentration. The residence chamber temperature was maintained at 150° C. A 10% standard deviation with four repeating samples was reported by the testing facility.

The mercury capture efficiency (%) was defined by Equation 1 and Equation 2 as set forth above. The in-flight mercury capture was measured with a drop-tube reactor. The carrier gas was the actual flue gas duct-piped from the boiler. The mercury species in the flue gas has a distribution of about 70% elemental mercury and 30% ionic mercury.

Table 5 lists the in-flight capture test data for selected blended preparations of brominated 13X zeolite and Darco-Hg at 4 lb/Mmacf injection rate. For nonblended sorbents with 10 and 7% Br loading (Samples 1 and 2), the total mercury capture, Hg(T), was about 65 and 75% at 2 and 4 second residence time, respectively. Adding 10% Darco-Hg to 10% Br 13X zeolite or 20% Darco-Hg to 7% Br 13X zeolite (Samples 3 and 4) actually caused a decrease of Hg(T). Surprisingly, adding 20% of Darco-Hg in 10% Br 13X zeolite (Sample 5) resulted in a significant increase of Hg(T) to about 86 and 82% at 2 and 4 seconds, respectively.

TABLE 5

Effect of Activated Carbon on the in-flight mercury capture of Selected Brominated 13X Zeolite Preparations

Sample	Br in 13X Zeolite, %	PAC (Darco-Hg) in blend, %	Total Mercury Capture, % Residence Time 2.0 sec	Total Mercury Capture, % Residence Time 4.0 sec
1	10	0	64	76
2	7	0	65	75

TABLE 5-continued

Effect of Activated Carbon on the in-flight mercury capture of Selected Brominated 13X Zeolite Preparations

Sample	Br in 13X Zeolite, %	PAC (Darco-Hg) in blend, %	Total Mercury Capture, % Residence Time 2.0 sec	Total Mercury Capture, % Residence Time 4.0 sec
3	10	10	60.0	65.0
4	7	20	60.3	60.3
5	10	20	86.0	82.0

FIG. **3** shows the total mercury capture of Samples 2 (without activated carbon) and 5 (with activated carbon) at 2 second residence time at different injection rates. For unblended 7% Br 13X zeolite (Sample 2), the mercury capture expectedly increased as the sorbent injection rate was increased from 2 to 4 lb/Mmacf. However, the mercury capture fell sharply at 8 lb/Mmacf possibly due to agglomeration of the sorbent particles when the sorbent passed through the screw feeder. On the other hand, the blend of 10% Br 13X zeolite and 20% Darco-Hg (Sample 5) showed a high total mercury capture up to 95% at 8 lbs injection rate. Overall, FIG. **3** shows that a blend of 20% of a flow modifier with halogenated particles of a mineral sorbent substrate can produce a sorbent composition which exhibits a total mercury capture of about 85% to 95% at injection rates of 4-8 lb/Mmacf. Thus, the activated carbon not only contributed to the overall mercury capture, but also served as a flow modifier to help reduce the agglomeration of brominated 13X zeolite particles at high injection rate and enhance overall mercury capture.

With a larger spray drier, more brominated 13X zeolite samples were prepared. The spray drier outlet temperature was maintained at 150° C. A typical slurry for spray drying consisted of 100 lbs. NaBr, 1100 lbs. of 13X zeolite and water. The brominated sorbent was then blended with different activated carbons that were Br-free (obtained from Jacobi Carbon and Norit, Samples 6 and 7). The samples were measured for their mercury capture efficiency. Table 6 lists the mercury capture results by the Apogee slipstream field measurement. Both blended samples (Sample 6 ad Sample 7) contained 8.0 wt % Br in the brominated sorbent and 20 wt % of activated carbon of the total blend. The drop-tube slipstream reactor was kept at 150° C. A pure brominated activated carbon (Sample 8), Darco Hg-LH from Norit, was used as a reference.

TABLE 6

Effect of different activated carbons in blended sorbents on in-flight mercury capture

Sample	Carbon Source	Feed Rate lb/MMacf	Total Mercury Capture % Residence Time 2.0 sec.	Total Mercury Capture % Residence Time 4.0 sec.
6a	Jacobi Carbon (AquaSorb 500P)	1	77	87
6b	Jacobi Carbon (AquaSorb 500P)	2	89	94
7	Norit (FGD)	2	92	96
8 (reference)	Norit (Darco-Hg-LH	2	94	97

Beside the Examples provided above on a blend of brominated (or other oxidatively active halide) zeolite (or other mineral substrate particle) with a non-brominated activated

carbon, blends of brominated activated carbon with a non-brominated zeolite or blends of brominated zeolite and brominated activated carbon can also be used. Besides physically blending, the activated carbon and zeolite can first be blended, followed by bromination of the mixture. Furthermore, when using bromides and 13X zeolite, another mineral substrate particle, such as FCC fines, may be blended in at any preferred ratio to reduce the cost of the oxidative sorbent preparation.

Example 22

Evaluation of Sorbent Preparation Methods

To evaluate the contribution of activated carbon per se to the overall mercury capture vs. its contribution by enhancement of the sorbent flowability, 20% PAC can be mixed with 13X zeolite and NaBr (10% Br), and then spray dried. The addition of 20% PAC to the mineral sorbent in this manner is not expected to yield a higher mercury capture as do compositions in which the mineral sorbent is physically blended PAC either before or after halogenation. This experiment will demonstrate that when the advantageous flow characteristic properties of the activated carbon are substantially compromised by the manufacturing method, its effectiveness as a flow modifier in the compositions of the invention are also reduced with a corresponding reduction in the mercury capture capabilities of the inventive compositions. That is, it is the flow enhancement obtained by physically blending PAC with the mineral substrate particles that yields the significant improvement in mercury capture.

As used herein, the term “physically blended” and variations thereof refer to a process or composition wherein discrete particles of the mineral substrate component are mixed with discrete particles of the flow modifier component. Although there may be chemical species exchanged between the mineral sorbent and the flow modifier particles, such as a migration of some halogen anions from the mineral substrate to the flow modifier particles, the physical blending does not substantially compromise the flow characteristics of the flow modifier component. By physical blending, the flow modifier helps reduce the agglomeration and enhance the flow characteristic the mineral sorbent particles. Halogenation may be performed on one or more of the components prior to mixing or it may be performed on the mixture.

Example 24

Non-Carbon Flow Modifiers

To evaluate a non-activated carbon flow modifier, 20% graphite was physically blended to Sample 1 (Sample 7) and tested for mercury capture. The graphite was purchased from Aldrich and has very little porosity. Yet, the mercury capture of Sample 7 is much higher than that of Sample 1, 74 and 79% at 2 and 4 second residence time and 4 lbs/Mmacf sorbent injection rate. This results demonstrated again that the mercury capture performance of Sample 1, brominated zeolite, improved by a flow modifier, whether the flow modifier has high porosity or not. Similar results were obtained with other flow modifiers such as calcined clay microspheres, surface treated clay produced by acid or organic coating, alumina, pseudo boehmite, silica, and their mixtures with activated carbon. Even with the low porosity of the graphite, performance was improved compared to mineral sorbent alone, although not as effective as activated carbon. This result may be because the flow characteristics of graphite are not as good as activated carbon.

Example 25

Cement Foaming Index Measurement

The concrete compatibility of the blended sorbent compositions was measured by the foaming index. This is a simple and preliminary indicator of how an additive impacts the air entrainment admixture for a cement. Ideally, after addition of any additive to cement, its foaming index should not change significantly. More specifically, the number of drops of the air entrainment admixture required to produce a stable foam should be below about 20-30. The control cement used in the foaming index measurement is Cemex Type I Portland. The air entrainment admixture is BASF MB VR standard at 1:10 dilution, the fly ash is a Class C PRG combustion product. In a typical experiment, 1.0 wt % (which is approximately equivalent to 4 lb/MMacf injection rate) of the sorbent was physically blended with the fly ash and the mixture was then added to the cement. For comparison, a pure activated carbon was also physically blended with the fly ash and then tested for its foaming index. Table 7 shows that adding fly ash, fly ash plus Br/13X, or fly ash plus Br/13X with up to 20% PAC blend yielded an acceptable foaming index. The results demonstrate that the blended mercury capture sorbent of the present invention, exemplified by a Br/zeolite+flow modifier, is compatible with concrete applications when the blend sorbent-latent fly ash is used as a concrete additive. On the other hand, as shown in Table 7, dramatic increases and an unacceptable level of foaming index were observed when the pure carbon (Norit Darco Hg-LH) was used instead of the mineral-based sorbent, which greatly limits the use of pure activated carbon injection for mercury emission control from coal-fired flue gas.

TABLE 7

Effect of sorbent additive on cement foaming index

Sample	Cement + Additive	# drops to produce stable foam Test 1	Test 2	Test 3
11	Cement control	4	3	3
12	Cement + fly ash	6	5	6
13	Cement + fly ash + 7% Br/13X	7	6	5
14	Cement + fly ash + 7% Br/13X + 20% Jacobi AquaSorb 500P	9	9	9
15	Cement + fly ash + 10% Br/13X + 10% Jacobi AquaSorb 500P	7	6	5
16	Cement + fly ash + 10% Br/13X + 20% Jacobi AquaSorb 500P	10	10	11
17	Cement + fly ash + 10% Br/13X + 20% Norit FGD	9	10	9
18	Cement + fly ash + Norit Darco Hg-LH	60	63	62

Example 26

Mass Balance Measurement

To quantitatively measure the agglomeration of brominated mineral particles and to evaluate how a physically blended flow modifier can reduce the agglomeration, a mass balance study was conducted by Illinois Institute of Technology using an acoustically driven aerosol injection method. The experimental setup was described in detail elsewhere [E. M. Lee and H. L. Clack, Agglomeration and Triboelectric Charging, 2009 EUEC]. Briefly, the experimental configuration features an acoustically driven aerosol generation chamber designed to impulsively eject a preset mass of powder in the form of a particle-laden jet. Humidity in the chamber is maintained at 0%. An acoustic transducer is mounted to one side of the chamber and is driven by an amplified signal controlled by a function generator. Once the desired mass of powdered sorbent is added to the chamber, the acoustic transducer sonicates the chamber and its contents, simultaneously forming a particle suspension from the powder and impulsively ejecting the suspension through a small nozzle to form a particle-laden jet. The ejected powder is captured in a HEPA filter and weighed after each test. The mass balance between the powder injected into and coming out of the aerosol generation chamber, and the number of injections required to reach an equilibrium value of mass balance can be used as a measurement of the degree of agglomeration of the powder particles.

FIG. **4** shows the mass balance measurement results of several sorbents with and without a PAC flow modifier.

As shown in FIG. **4**, it took about 5 injections for an activated carbon reference (Darco-HG) to reach a mass balance of about 70%. Sample 1 (Br/13X) never reached a mass balance above 40% even after 20 injection, a clear indication of a severe particle agglomeration. Adding 10% PAC in Br/13X (Sample 3) increased the mass balance slowly to above 80% after about 20 injections. Adding 20% PAC in Br/13X (Sample 5) dramatically reduced the number of injections to 3 to reach a mass balance of 80%. Substituting 13X zeolite with FCC fine particles also yielded a good mass balance. The mass balance measurement data is consistent with the mercury capture data in Table 5. It provides evidence that adding PAC in brominated zeolite significantly reduce the agglomeration of sorbent particles and increases its flowability.

Beside the Examples provided above on a blend of brominated (or other oxidatively active halide) zeolite (or other mineral substrate particle) with a non-halogenated activated carbon, physical blends of halogenated flow modifier with a non-halogenated mineral substrate or physical blends of halogenated mineral substrate and halogenated flow modifier can also be used. As an alternative to physically blending the components after halogenation, the flow modifier and the mineral substrate can first be physically blended, followed by halogenation of the mixture. Furthermore, when using bromides and a zeolite such as 13X, another mineral substrate particle, such as FCC fines, may be blended in at any preferred ratio to reduce the cost of the oxidative sorbent preparation.

It will be apparent to those skilled in the art that various modifications and variations can be made to the present invention without departing from the spirit or scope of the invention. For example, while the sorbents disclosed herein are particularly useful for removal of mercury from the flue gas of coal-fired boilers, the sorbents can be used to remove heavy metals such as mercury from other gas streams, including the flue gas of municipal waste combustors, medical waste incinerators, and other Hg-emission sources. Thus, it is intended that the present invention cover modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

What is claimed is:

1. A sorbent composition for removal of mercury from a flue gas, the sorbent composition comprising:

one or more bromides of a nonoxidative metal dispersed on porous particles, wherein the nonoxidative metal is selected from the group consisting of sodium, potassium, calcium, magnesium, and combinations thereof, and wherein the one or more bromides are dispersed on the porous particles according to a drying process; and

a flow modifier physically blended with the porous particles in an amount sufficient to reduce agglomeration of the porous particles when injected into the flue gas, wherein the porous particles are selected from the group consisting of alumina, silica, titania, zirconia, iron oxides, zinc oxide, rare earth oxides, metal carbonate, metal sulfate, aluminosilicates, zeolites, clays, heat-treated clays, chemical-surface modified clays, talc, fly ash, fluid cracking catalyst (FCC) particles, dirt, and combinations thereof.

2. The sorbent composition of claim **1**, wherein the bromide is present in an amount of 0.1% by weight to 30% by weight of the porous particles.

3. The sorbent composition of claim **1**, wherein the bromide is present in an amount of 1.56% by weight to 6% by weight of the porous particles.

4. The sorbent composition of claim **1**, wherein the flow modifier is present in an amount of about 10% to about 30% by weight of the sorbent composition.

5. The sorbent composition of claim **1**, wherein the flow modifier is present in an amount of about 10% to about 20% by weight of the sorbent composition.

6. The sorbent composition of claim **1**, wherein the flow modifier comprises powdered activated carbon.

7. The sorbent composition of claim **6**, wherein the porous particles are selected from the group consisting of clays, heat-treated clays, chemical-surface modified clays, kaolin and heat treated kaolin.

8. The sorbent composition of claim **1**, wherein the nonoxidative metal is selected from the group consisting of sodium, calcium and combinations thereof.

9. The sorbent composition of claim **1**, wherein the flow modifier comprises powdered activated carbon and is present in an amount of about 10% to about 20% by weight of the sorbent composition.

10. The sorbent composition of claim **1**, wherein the flow modifier is present in amount from about 10% to about 30% by weight of the sorbent composition and the porous particles are selected from the group consisting of kaolin, heated treated kaolin, chemical-surface modified kaolin, and combinations thereof.

11. The sorbent composition of claim **10**, wherein the nonoxidative metal is sodium.

12. The sorbent composition of claim **10**, wherein the flow modifier comprises powdered activated carbon.

13. The sorbent composition of claim **12**, wherein the powdered activated carbon is present in amount of about 10% to about 20% of the sorbent composition.

14. The sorbent composition of claim **1**, wherein an average size of the porous particles is less than 100 micrometers.

15. The sorbent composition of claim **1**, wherein the bromide is present in an amount of 0.1% by weight to 15% by weight of the porous particles.

16. A sorbent composition for removal of mercury from a flue gas, the sorbent composition comprising:

one or more bromides of a nonoxidative metal dispersed on porous particles, wherein the nonoxidative metal is selected from the group consisting of sodium, potassium, calcium, magnesium, and combinations thereof, and wherein the one or more bromides are dispersed on the porous particles according to a drying process; and

a flow modifier physically blended with the porous particles in an amount sufficient to reduce agglomeration of the porous particles when injected into the flue gas, wherein the flow modifier comprises powdered activated carbon and is present in an amount of about 10% to about 30% by weight of the sorbent composition.

* * * * *